PROCESS FOR THE MANUFACTURE OF 1,3,3,3-TETRAFLUOROPROPENE

BACKGROUND OF THE INVENTION

This invention relates a process for the manufacture of 1,3,3,3-tetrafluoropropene (HFC-1234ze). More particularly, the invention pertains to a process for the manufacture of HFC-1234ze by a two stage vapor phase process. The process comprises a hydrofluorination of 1-chloro-3,3,3-trifluoropropene (HCFC-1233zd) into 1-chloro-1,3,3,3-tetrafluoropropane (HCFC-244fa) and 1,1,1,3,3-pentafluoropropane (HFC-245fa), followed by the dehydrochlorination of HCFC-244fa and dehydrofluorination of HFC-245fa.

Traditionally, chlorofluorocarbons (CFCs) like trichlorofluoromethane and dichlorodifluoromethane have been used as refrigerants, blowing agents and diluents for gaseous sterilization. In recent years, there has been widespread concern that certain chlorofluorocarbons might be detrimental to the Earth's ozone layer. As a result, there is a worldwide effort to use halocarbons which contain fewer or no chlorine substituents. Accordingly, the production of hydrofluorocarbons, or compounds containing only carbon, hydrogen and fluorine, has been the subject of increasing interest to provide environmentally desirable products for use as solvents, blowing agents, refrigerants, cleaning agents, aerosol propellants, heat transfer media, dielectrics, fire extinguishing compositions and power cycle working fluids. In this regard, 1,3,3,3-tetrafluoropropene (HFC-1234ze) is a compound that has the potential to be

used as a zero Ozone Depletion Potential (ODP) and a low Global Warming Potential (GWP) refrigerant, blowing agent, aerosol propellant, solvent, etc, and also as a fluorinated monomer.

5   It is known in the art to produce HFC-1234ze. For example, U.S. Patent 5,710,352 teaches the fluorination of 1,1,1,3,3-pentachloropropane (HCC-240fa) to form HCFC-1233zd and a small amount of HFC-1234ze. U.S. patent 5,895,825 teaches the fluorination of HCFC-1233zd to form HFC-1234ze. U.S. patent 6,472,573 also teaches the fluorination of HCFC-1233zd

10   to form HFC-1234ze. U.S. patent 6,124,510 teaches the formation of cis and trans isomers of HFC-1234ze by the dehydrofluorination of HFC-245fa using either a strong base or a chromium-based catalyst. Additionally, European patent EP 0939071 describes the formation of HFC-245fa via the fluorination of HCC-240fa through intermediate reaction product which is an azeotropic

15   mixture of HCFC-1233zd and HFC-1234ze.

It has been determined that these known processes are not economical relative to their product yield. Accordingly, the present invention provides an alternate process for forming HFC-1234ze which is more economical than

20   prior art processes and at a higher yield as compared to known processes. In particular, it has now been found that HFC-1234ze may be formed by a two step reaction involving the hydrofluorination of 1-chloro-3,3,3-trifluoropropene (HCFC-1233zd) into 1-chloro-1,3,3,3-tetrafluoropropane (HCFC-244fa) and subsequent fluorination of the HCFC244fa to form

25   1,1,1,3,3-pentafluoropropane (HFC-245fa), followed by the dehydrochlorination of HCFC-244fa and dehydrofluorination of HFC-245fa via reaction with a caustic solution. Alternately, the dehydrochlorination of HCFC-244fa and dehydrofluorination of HFC-245fa may be undertaken by thermal decomposition in the absence of or in the presence of a catalyst.

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DESCRIPTION OF THE INVENTION

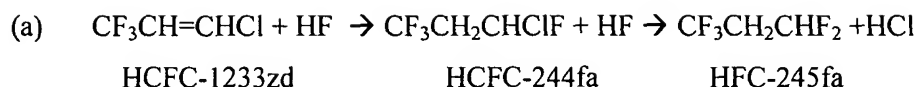The invention provides a process for the manufacture of 1,3,3,3-tetrafluoropropene comprising :

5   a) reacting 1-chloro-3,3,3-trifluoropropene with hydrogen fluoride in a reactor in the vapor phase and in the presence of a fluorination catalyst and under conditions sufficient to form an intermediate product which comprises 1-chloro-1,3,3,3-tetrafluoropropane and/or 1,1,1,3,3-pentafluoropropane; and

b) reacting said intermediate product with a caustic solution and under

10   conditions sufficient to dehydrochlorinate 1-chloro-1,3,3,3-tetrafluoropropane and/or to dehydrofluorinate 1,1,1,3,3-pentafluoropropane, forming a reaction product which comprises 1,3,3,3-tetrafluoropropene.

The invention also provides a process for the manufacture of 1,3,3,3-

15   tetrafluoropropene comprising :

a) reacting 1-chloro-3,3,3-trifluoropropene with hydrogen fluoride in a reactor in the vapor phase and in the presence of a fluorination catalyst and under conditions sufficient to form an intermediate product which comprises 1-chloro-1,3,3,3-tetrafluoropropane and/or 1,1,1,3,3-pentafluoropropane; and

20   b) thermally decomposing said intermediate product under conditions sufficient to dehydrochlorinate 1-chloro-1,3,3,3-tetrafluoropropane and/or to dehydrofluorinate 1,1,1,3,3-pentafluoropropane, forming 1,3,3,3-tetrafluoropropene.

25   The first step (a) of the process of the invention involves the formation of 1-chloro-1,3,3,3-tetrafluoropropane (HCFC-244fa) and 1,1,1,3,3-pentafluoropropane (HFC-245fa) by reacting 1-chloro-3,3,3-trifluoropropene (HCFC-1233zd) with hydrogen fluoride (HF) in the vapor phase, preferably in the presence of a fluorination catalyst. This reaction proceeds as follows:

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(a) $CF_3CH=CHCl + HF \rightarrow CF_3CH_2CHClF + HF \rightarrow CF_3CH_2CHF_2 + HCl$
         HCFC-1233zd   HCFC-244fa   HFC-245fa

The result is a reaction mixture of the two reaction products, HCFC-244fa and HFC-245fa. In the preferred embodiment of the invention, the mole ratio of HF to HCFC-1233zd for this reaction preferably ranges from about 1:1 to about 50:1, more preferably from about 2:1 to about 30:1 and most preferably from about 3:1 to about 20:1.

The 1-chloro-3,3,3-trifluoropropene (HCFC-1233zd) employed may be either solely the trans isomer form, or solely the cis isomer form or a combination of both the trans and cis isomers forms. In one embodiment, the HCFC-1233zd comprises from about 60% to about 100% of the trans isomer form with the balance being the cis isomer form. In another embodiment, the HCFC-1233zd comprises from about 70% to about 100% of the trans isomer form with the balance being the cis isomer form. In yet another embodiment, the HCFC-1233zd comprises from about 80% to about 100% of the trans isomer form with the balance being the cis isomer form.

Preferred fluorination catalysts include, but are not limited to, transition metal halides, Group IVb and Vb metal halides, and combinations thereof, preferably supported on activated carbon or fluorinated alumina. More specifically, preferred fluorination catalysts non-exclusively include $SbCl_5$, $SbCl_3$, $TaCl_5$, $SnCl_4$, $NbCl_5$, $TiCl_4$, $MoCl_5$, Cr_2O_3/Al_2O_3, Cr_2O_3/AlF_3, $Cr_2O_3/carbon$, $CoCl_2/Cr_2O_3/Al_2O_3$, $NiCl_2/Cr_2O_3/Al_2O_3$, $CoCl_2/AlF_3$, $NiCl_2/AlF_3$ and mixtures thereof, where it is understood that after pre-treatment with HF or during reaction in the presence of HF the above mentioned catalyst will be partially fluorinated The preferred catalysts are $SbCl_3$ and $SbCl_5$ halides supported on activated carbon. Fluorination catalysts having a purity of at least 98% are preferred. The fluorination catalyst is present in an amount

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sufficient to drive the reaction. The fluorination reaction may be conducted in any suitable fluorination reaction vessel or reactor but it should preferably be constructed from materials which are resistant to the corrosive effects of hydrogen fluoride such as nickel and its alloys, including Hastelloy, Inconel,

5   Incoloy, and Monel or vessels lined with fluoropolymers.

Any water in the hydrogen fluoride (HF) will react with and deactivate the fluorination catalyst. Therefore substantially anhydrous hydrogen fluoride is preferred. By "substantially anhydrous" it is meant that the HF contains less

10   than about 0.05 weight % water and preferably contains less than about 0.02 weight % water. However, one of ordinary skill in the art will appreciate that the presence of water in the HF can be compensated for by increasing the amount of catalyst used.

15   The reaction of step (a) is preferably conducted at a temperature of from about 50°C to about and 200°C, more preferably from about 60°C to about 180°C and most preferably from about 65°C and 150°C. Step (a) is also preferably conducted at a pressure of from about 15 psia to about 215 psia, more preferably from about 15 psia to about 165 psia and most preferably from

20   about 30 psia to about 100 psia. In the process of the invention, the reactor is preferably preheated to the desired fluorination reaction temperature while anhydrous HF is fed to the reactor. The HCFC-1233zd and HF may be fed to the reactor at the desired temperatures and pressures that are described herein. In a preferred embodiment of the invention, either or both of the HCFC-

25   1233zd and HF are pre-vaporized or preheated prior to entering the reactor. Alternately, the HCFC-1233zd and HF are vaporized inside the reactor. During the fluorination reaction, HCFC-1233zd and HF are reacted in a vapor phase with the fluorination catalyst. The reactant vapor is allowed to contact the fluorination catalyst for from about 0.01 to about 240 seconds, more
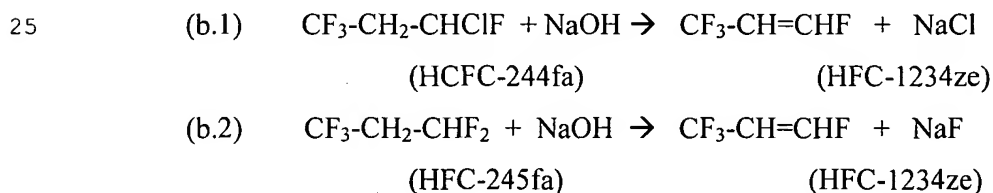
preferably from about 0.1 to about 60 seconds and most preferably from about 0.5 to about 20 seconds.

In the preferred embodiment, the process flow of step (a) is in the down direction through a bed of the catalyst. Before each use, the catalyst is preferably dried, pre-treated and activated. It may also be advantageous to periodically regenerate the catalyst after prolonged use while in place in the reactor. For Cr_2O_3, Cr_2O_3/Al_2O_3, Cr_2O_3/AlF_3, $Cr_2O_3/carbon$, $CoCl_2/Cr_2O_3/Al_2O_3$, $NiCl_2/Cr_2O_3/Al_2O_3$, $CoCl_2/AlF_3$, $NiCl_2/AlF_3$ catalysts, pre-treatment can be done by heating the catalyst to about 250 °C to about 430 °C in a stream of nitrogen or other inert gas. The catalyst may then be activated by treating it with a stream of HF diluted with a large excess of nitrogen gas in order to obtain high catalyst activity. Regeneration of the catalyst may be accomplished by any means known in the art such as, for example, by passing air or air diluted with nitrogen over the catalyst at temperatures of from about 100°C to about 400°C, preferably from about 200°C to about 375°C, for from about 1 hour to about 3 days, depending on the size of the reactor. For $SbCl_5$, $SbCl_3$, $TaCl_5$, $SnCl_4$, $NbCl_5$, $TiCl_4$, $MoCl_5$ catalysts, supported on an solid support such as activated carbon, pre-treatment or activation can be done by first heating the catalyst to about 30°C to 250°C in a stream of nitrogen or other inert gas. It is then treated with a stream of HF in the absence or presence of an oxidizing agent such as chlorine gas in order to obtain high catalyst activity. In addition, the catalyst may optionally be kept active by co-feeding chlorine to the reactor during reaction.

HCFC-244fa and HFC-245fa may be recovered from the fluorination reaction product mixture comprised of unreacted starting materials and by-products, including HCl, by any means known in the art, such as by extraction and preferably distillation. For example, the distillation may be preferably conducted in a standard distillation column at a pressure which is less than

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about 300 psig, preferably less than about 150 psig and most preferably less than 100 psig. The pressure of the distillation column inherently determines the distillation operating temperature. HCl may be recovered by operating the distillation column at from about -40 °C to about 25 °C, preferably from about

5   -40 °C to about -20°C. Single or multiple distillation columns may be used. The distillate portion includes substantially all the HCFC-244fa, HFC-245fa, unreacted HF and HCl produced in the reaction as well as any other impurities. In the preferred embodiment, HCFC-244fa and the HFC-245fa are separated from all other reaction by-products and unreacted HF for further

10 reaction in step (b) described herein. In the preferred embodiment, any HF present may also be recovered and recycled back for subsequent fluorination reactions.

Once reaction step (a) is completed, the second step (b) is the conversion of

15 the reaction mixture obtained from (a), which contains substantially HCFC-244fa and HFC-245fa, to HFC-1234ze. As the reaction formulas below illustrate, HFC-1234ze is formed by the dehydrochlorination of HCFC-244fa and the dehydrofluorination of HFC-245fa. In the preferred embodiment of the invention, the dehydrochlorination of HCFC-244fa and ·

20 dehydrofluorination of HFC-245fa are accomplished by reacting each of these respective intermediates with a strong caustic solution that includes, but is not limited to KOH, NaOH, Ca(OH)$_2$ and CaO at an elevated temperature. This reaction proceeds, for example, as follows:

25   (b.1) $CF_3\text{-}CH_2\text{-}CHClF + NaOH \rightarrow CF_3\text{-}CH=CHF + NaCl$
                        (HCFC-244fa)   (HFC-1234ze)
            (b.2) $CF_3\text{-}CH_2\text{-}CHF_2 + NaOH \rightarrow CF_3\text{-}CH=CHF + NaF$
                        (HFC-245fa)   (HFC-1234ze)

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Dehydrochlorination and dehydrofluorination reactions are well known in the art. In the preferred embodiment of the invention, the caustic strength of the caustic solution is of from about 2 wt % to about 100 wt %, more preferably from about 5 wt % to about 90 wt % and most preferably from about 10 wt % to about 80 wt %. The reaction is preferably conducted at a temperature of from about 20°C to about 100°C, more preferably from about 30°C to about 90°C and most preferably from about 40°C to about 80°C. The reaction is preferably conducted at atmospheric pressure, super-atmospheric pressure or under vacuum. The vacuum pressure can be from about 5 torr to about 760 torr. In addition, a solvent may optionally be used to help dissolve the organic compounds in the caustic solution. This optional step may be conducted using solvents that are well known in the art for said purpose.

In an alternate embodiment of the invention, the dehydrochlorination of HCFC-244fa and dehydrofluorination of HFC-245fa may be done by thermal decomposition in the presence or in the absence of a catalyst. Suitable catalysts include transition metal halides, supported or bulk. Preferred catalyst include, but are not limited to, $FeCl_3$, $NiCl_2$, $CoCl_2$, supported or in bulk. The preferred temperatures for the thermal decomposition are from about 30°C to about 400°C, more preferably from about 50°C to about 350°C and most preferably from about 75°C to about 300°C. As above, the reaction is preferably conducted at atmospheric pressure, super-atmospheric pressure or under vacuum. The vacuum pressure can be from about 5 torr to about 760 torr.

The reactions of both step (a) and step (b) may be conducted in any suitable reactor. Further, the dehydrochlorination of 1-chloro-1,3,3,3-tetrafluoropropane (HCFC-244fa) and the dehydrofluorination of 1,1,1,3,3-pentafluoropropane (HFC-245fa) may either be conducted simultaneously in the same reactor, or they may first be separated followed by separately dehydrochlorinating 1-

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chloro-1,3,3,3-tetrafluoropropane with said caustic solution or by thermal decomposition and separately dehydrofluorinating 1,1,1,3,3-pentafluoropropane with said caustic solution or by thermal decomposition. The result of this two step process is a high yield of HFC-1234ze.

The following non-limiting examples serve to illustrate the invention.

EXAMPLES 1-18

The fluorination reaction was conducted in a 2.54 cm diameter, 81 cm long Monel® reactor. The reactor was heated with an electric furnace. The reactants of HCFC-1233zd (>99.9% purity), anhydrous HF and, optionally, chlorine, were fed to the reactor at constant flow rates. The flow rate of the chlorine was measured using a Hasting mass flow meter and controller. The flow rate for the reactants, HCFC-1233zd and HF, were controlled and measured by Honeywell PlantScape DCS (Distributive Control System) and confirmed by the weight change in the respective source cylinders.

The reactor output was sampled directly into an in-line GC, i.e. a Perkin Elmer 8500 gas chromatograph, using a Fluorocol column and FID detector, so that the amounts of organic species exiting the reactor could be determined during the operation of the process.

The reaction conditions for Examples 1-18 and corresponding experimental results are listed below in Tables1 and 2, respectively. Contact time is defined as bulk volume (in ml) of catalyst divided by volumetric flow rate of reactants (in ml/sec).

Preparation of catalyst 1 and 2 are described below:

Catalyst 1

5   This catalyst was made by impregnating SbCl$_5$ (250 g) on granular Shiro Sagi
     G2X (4 x 6 mesh) activated carbon (500 ml). It was charged to the reactor and
     activated in the reactor before use. Activation procedures were as follows: at
     first, nitrogen of 20 ml/min was flowed over the catalyst. In this nitrogen
     atmosphere, the reactor was heated to 100°C. Then, anhydrous HF and
10   chlorine were allowed to flow through the reactor at 0.25 g/min and 0.3 g/min,
     respectively, for 30 minutes to 1 hour, depending on volume of catalyst. Once
     the activation is complete, the HF and chlorine flows were stopped and the
     catalyst was cooled to the desired reaction temperature under a nitrogen
     atmosphere.
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Catalyst 2
     This catalyst was made and activated using the same procedures as those for
     catalyst 1, except that Toyo Calgon PCB (4 x 10 mesh) activated carbon was
     used instead. The amounts of SbCl$_5$ and activated carbon used were 169 g and
20   340 ml, respectively.

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REACTION CONDITIONS

Example #	Catalyst	Pressure (psia)	Temp. °C	Contact Time (sec)	Cl_2/org mole ratio	HF/org mole ratio
1	1	15	80	4.6	0.0	10
2	1	15	80	8.9	0.0	10
3	1	15	80	27.4	0.0	10
4	2	15	80	0.9	0.0	10
5	2	15	80	1.9	0.0	10
6	2	15	80	6.3	0.0	10
7	2	30	65	1.1	0.015	10
8	2	30	65	2	0.015	10
9	2	30	65	10.1	0.015	10
10	2	30	85	1	0.015	10
11	2	30	85	1.9	0.015	10
12	2	30	85	9.5	0.015	10
13	2	60	85	2	0.015	10
14	2	60	85	5.2	0.015	10
15	2	60	85	10.4	0.015	10
16	1	45	70	1.5	0.015	10
17	1	45	70	2.5	0.015	10
18	1	45	70	11.5	0.015	10

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EXPERIMENTAL RESULTS

Example #	1234ze	Composition at Reactor Outlet 245fa	1233zd	244fa	Others
1	0.02	77.31	7.82	13.28	1.57
2	0.01	91.90	2.32	5.16	0.61
3	0.00	99.11	0.07	0.39	0.43
4	0.21	20.66	62.79	15.71	0.64
5	0.34	50.08	27.90	20.76	0.93
6	0.09	90.41	4.26	4.14	1.10
7	0.13	38.19	32.76	27.69	1.23
8	0.03	39.68	26.12	32.62	1.54
9	0.01	70.83	4.64	22.28	2.24
10	0.16	55.03	26.40	17.14	1.28
11	0.05	64.26	14.90	19.12	1.66
12	0.00	91.67	2.01	5.30	1.02
13	0.13	14.86	57.38	25.05	1.56
14	0.05	43.94	24.95	28.09	2.44
15	0.07	42.29	22.82	30.22	3.69
16	0.10	22.14	50.61	25.95	1.19
17	0.16	34.85	35.99	27.65	1.35
18	0.04	92.97	0.99	5.30	0.71

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The results showed that the shorter the contact time the more HCFC-244fa
was formed, indicating that 244fa is an intermediate from the reaction of
1233zd with HF to make HFC-245fa. Process conditions using shorter contact

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time are preferred, because HFC-1234ze made from 244fa is cheaper and easier than that from 245fa.

The unreacted 1233zd and HF can be recycled back to the reactor to make more 244fa and 245fa.

EXAMPLE 19

A starting material consisting of 91.5 GC area % 1,1,1,3,3-pentafluoropropane (HFC-245fa) and 0.0121 GC area % HFC-1234ze was bubbled through a 2.0 wt% potassium hydroxide (KOH) solution. The organic mixture resulting from the combination was collected and analyzed by GC equipped with a FID. The mixture contained 15.455 GC area % HFC-1234ze.

EXAMPLE 20

To a reaction setup consisting of a 3-neck round bottom flask (5 L), mechanical agitator, reflux condenser, and low temperature cold trap was added to 3000 ml acetonitrile and 9.9 moles (504 g) of KOH pellets. After mixing, 5.1 moles (684 g) of 80 GC area % HFC-245fa/20 GC area% HCFC-1233zd was added through a dip leg. The reagents were heated slowly with vigorous agitation. Reaction was observed at about 60°C. The crude product was collected in the cold finger. The crude material was analyzed by GC and consisted of about 62.0 GC area % HFC-1234, 20.9 GC area % HFC-245fa, and 16.2 GC area % HCFC-1233zd.

EXAMPLE 21

539.5 grams of 9.3 wt % KOH solution and 135.4 grams of 90.0 GC area % pure 1-chloro-1,3,3,3-tetrafluoropropane (HCFC-244fa) were added to a 1.0

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liter SS cylinder. The other major component was HCFC-1223xd which amounted to 9.2 GC area %. The cylinder was heated to 75 – 80 °C and shaken for five (5) hours. A sample of the vapor space showed the presence of 75.6 area % HFC-1234ze trans isomer, 12.9 area % HFC-1234ze cis isomer,

5   8.5 GC area % HCFC-244fa, and 0.8 GC area % HCFC-1223xd. A sample of the organic liquid phase showed 24.4 GC area % HFC-1234ze trans isomer, 12.9 GC area % HFC-1234ze cis isomer, 44.2 GC area % HCFC-244fa, and 8.1 GC area % HCFC-1223xd.

10   560.0 grams of aqueous solution was collected after the experiment which amounts to a weight gain of 20.5 grams in the aqueous layer. Assuming this weight gain is HCl that was produced during the dehydrochlorination of 244fa it can be calculated that about a 60% conversion of HCFC-244fa to HFC-1234ze occurred during the reaction.

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EXAMPLE 22

In a typical experiment, a 2.54 cm x 81 cm Monel® reactor is used. About 500 ml of $FeCl_3$ catalyst supported on activated carbon was packed into the reactor. The reactor was heated to 150 °C under 1 liter/hr of nitrogen flow to

20   dry the catalyst for 4 hours. Then, the reactor temperature is brought to 250°C under the same nitrogen flow and 244fa is fed to the reactor at 1 g/min, and in the mean time the nitrogen flow is stopped. HFC-1234ze was found by using the in-line GC at the outlet of the reactor at 98% selectivity and 95% single pass conversion.

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EXAMPLE 23

The same experiment described in Example 22 is repeated, except that 245fa is used as feed. At the outlet of the reactor, 1234ze is found at 95% selectivity and 85% single pass conversion.

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While the present invention has been particularly shown and described with reference to preferred embodiments, it will be readily appreciated by those of ordinary skill in the art that various changes and modifications may be made without departing from the spirit and scope of the invention. It is intended that
10 the claims be interpreted to cover the disclosed embodiment, those alternatives which have been discussed above and all equivalents thereto.